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(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: MOSS, Michael, Alan, John [GB/GB]; 13 Painshawfield Road, Stockfield, Northumberland NE43 7DZ (GB). CLARE, Jonathan, Richard [GB/GB]; 55 Sanderson Road, Jesmond, Newcastle upon Tyne NE2 2DR (GB). SIMPSON, Anthony, Joseph [GB/GB]; 17 Sheringham Drive, Cramlington, Northumberland NE23 8HB (GB).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

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(54) Title: DETERGENT COMPONENT COMPRISING METAL ION-CONTAINING CRYSTALLINE LAYERED SILICATE

(57) Abstract

There is provided in a detergent component comprising in combination (a) a crystalline layered silicate; and (b) a metal ion, wherein said metal ion is present in the crystalline structure of the crystalline layered silicate. The detergent component provide an improved bleachable stain removal and an improved dye transfer inhibition.

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DETERGENT COMPONENT COMPRISING METAL ION-CONTAINING CRYSTALLINE LAYERED SILICATE.

Technical field

This invention relates to a detergent component comprising a crystalline layered silicate and additionally a metal ion for use in a washing method to achieve improved bleachable stain removal and dye transfer inhibition.

Background to the invention

The satisfactory removal of bleachable soils/stains such as tea, fruit juice and coloured vegetable soils from stained fabrics is a particular challenge to the formulator of a bleaching composition for use in a laundry washing method.

Traditionally, the removal of such bleachable stains has been enabled by the use of bleach components such as oxygen bleaches, including hydrogen peroxide and organic peroxyacids. The organic peroxyacids are often obtained by the in situ perhydrolysis reaction between hydrogen peroxide and an organic peroxyacid bleach precursor. More recently, products containing bleach catalysts, particularly transition metal-containing bleach catalysts have become of interest.

The inclusion of a bleach catalyst into a detergent composition may lead to a way to reduce the amount of bleach needed for bleachable stain removal. A challenge is to solve the problem of how to reduce the amount of bleach needed, whilst achieving a better bleachable stain removal, thereby optimising the bleach system.

In the present invention it is found that the above mentioned problem of optimising the bleach system can be achieved by inclusion in the detergent composition of a combined detergent component comprising a crystalline

layered silicate and a metal ion. The inclusion of this combined component provides a improved bleachable stain removal.

Another problem addressed by the present invention is the problem of dye transfer during the washing process. Dye transfer can occur during a washing process through the solution or transfer of dye-containing components of a fabric into the washing water. The dye-containing components in the washing water can then subsequently deposit on or transfer to (other) fabric. In the present invention it is found that the combined crystalline layered silicates and metal ions provide an improved dye transfer inhibition.

It is believed that the combined component comprising a crystalline layered silicate and a metal ion can form a complex or salt, once combined, which provides both the improvement of removal of the bleachable stains and the improvement of dye transfer inhibition.

Where present in detergent compositions not comprising a bleach system, the complex or salt formed by the combined detergent component comprising the crystalline layered silicate and the metal ion has been found to provide improved bleachable stain removal and dye transfer inhibition by chelation of components comprised in the stains and dyes.
Where present detergent compositions comprising a bleach system containing oxygen releasing compounds, the complex or salt formed by the combined detergent component is believed to catalyse the oxidised bleach reactions.

Bleach compositions including manganese containing bleach catalyst have been described, for example, in European Patent Applications EP-A-443,651, EP-A-544,490, EP-A-458,397, EP-A-458,398. These documents do not disclose the use of crystalline layered silicates in combination with a metal ion as a active complex or salt for bleachable stain removal and/ or dye transfer inhibition.

Crystalline layered silicates have been disclosed in EP-A-0164514 and their use in detergent compositions has been disclosed in DE-A-3413571 and DE-A-3812556. Preferred compositions including crystalline layered silicates and bleach components have been disclosed in PCT Patent Applications WO 94/03554 and EP-A-0640683. None of these documents recognise the use of a combination of crystalline layered silicates and a metal ion for improved bleachable stain removal and/or dye transfer inhibition.

The exchangeability of cations of a weak monoacidic base in aluminosilicates, such as zeolite, in a detergent composition comprising bleaching compositions is described in PCT Patent Application WO 94/24251. It does not recognise the use of layered silicates in combination with metal ions in detergent compositions for bleach performance and/or dye transfer inhibition.

A article in the 'Chemistry in Britain', November 1992 page 1006-1008, by Graham Hutchings, describes the use of titanium in zeolite complexes, as oxidation catalysts. It does not recognise the use of metal ions, such as titanium, in combination with crystalline layered silicates in detergent compositions.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

According to the present invention there is provided a detergent component comprising in combination

(a) a crystalline layered silicate; and

(b) a metal ion.

wherein said metal ion is present in the crystalline structure of said crystalline layered silicate.

Preferably, the crystalline layered silicate is a crystalline δ-layered silicate and most preferably it is a crystalline δ-layered sodium silicate with the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Most preferably the crystalline layered silicate has the formula δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6 (trade name).

The metal can be selected from a range of metal ions. The metal ion may vary in oxidation state. Preferably the metal ion is selected from the group of transition metals, comprising manganese, titanium, copper, cobalt, zinc and iron. Most preferably the selected transition metal ion is manganese II or titanium IV.

Detailed description of the invention

The crystalline layered silicate and metal ion combined component

The detergent component of the present invention contains a crystalline layered silicate in combination with a metal ion. The metal ion is present in the crystalline structure of the crystalline layered silicate material.
It has been found that the addition of this catalyst to a detergent composition provides for an improved bleachable stain removal and improved dye transfer inhibition.

The structure of the crystalline layered silicate is preferably a two dimensional 'sheet' structure, such as the so called δ-layered structure, as described in EP 0 164514 and EP 0 293640.

The preferred crystalline δ-layered silicate is a crystalline δ-layered sodium silicate with the general formula

$$NaMSi_xO_{2+1} \cdot yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20.

Preferably the crystalline layered sodium silicate has the formula δ-$Na_2Si_2O_5$, known as NaSKS-6 (trade name), available from Hoechst AG.

The concentration of the combined detergent composition, comprising crystalline layered silicate and a metal ion, is preferably from 5% to 30% by weight. Most preferably the concentration is from 10% to 25% by weight of the detergent composition.

The metal ion used in combination with the crystalline layered silicate can be selected from a range of metal. The oxidation state of the ion(s) may vary. Preferably the metal ion is a transition metal, more preferably the metal ion is selected from the group of transition metals, comprising manganese, titanium, copper, cobalt, zinc and iron. Most preferably the selected transition metal ion is manganese II or titanium IV.

The ratio of metal ions to the crystalline δ-layered silicate can be from 10 ppm to 1000 ppm, preferably from 20 ppm to 500 ppm by weight.

Preparation

The combined crystalline layered silicate and metal ion component in accord with the present invention can form a complex or salt by reaction. This can take place during the crystalline layered silicate synthesis, or in an aqueous solution with the crystalline layered silicate, or in organic solution with the crystalline layered silicate or with the crystalline layered silicate in situ.

Preferably the crystalline layered silicate is doped with the metal.
The synthesis of a transition metal complex or salt of the crystalline layered silicate by way of doping, is done by refluxing the crystalline layered silicate with a transition metal halide in a solvent, preferably an organic halide-containing solvent, whereafter the complex is obtained by purifying the reaction mixture.
The synthesis of a titanium or manganese containing complex or salt by way of doping is preferably done by refluxing the crystalline layered silicate with a halide salt of manganese or titanium, in dichloroethane solution (approximate 8 hours), whereafter the complex or salt is obtained by cooling, filtering and washing and removing excess solvent by desiccation.

Detergent composition

The detergent component of the claimed invention can be added to any detergent composition. Detergent compositions in accord with the invention may contain additional or optional detergent components. The precise nature of these additional or optional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

The detergent compositions of the invention preferably contain one or more detergent components selected from oxygen releasing bleach systems, surfactants, builders, organic polymeric compounds, additional enzymes,

suds suppressers, soil suspension and anti-redeposition agents and corrosion inhibitors.

Oxygen-releasing bleaching system

The detergent compositions in accordance with the claimed invention preferably contain an oxygen-releasing bleaching system containing essentially an oxygen bleaching species including for example, inorganic perhydrate bleaches and organic peroxyacids.

A preferred bleaching system contains a hydrogen peroxide source and a peroxyacid bleach precursor compound. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches.

The combined detergent component containing a crystalline layered silicate and a metal ion can catalyse the bleachable stain removal by interaction with the bleach system.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in compositions in accordance with the invention, is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is form 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes. Possible bleach precursors include

N-acylated lactams, perbenzoic acids, including the preferred precursor benzoyl oxybenzene sulfonate and perbenzoic acids of the imide type and phtalic anhydride.

Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds are also suitable herein. Typically such cationic peroxyacid precursors are formed by substituting the peroxyacid part with an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group.

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

Alkyl fatty peroxyacid bleach precursors

Alkyl fatty peroxyacid bleach precursors form alkyl fatty peroxyacids on perhydrolysis. Preferred precursors of this type give rise to peracetic acid on perhydrolysis.

Preferred alkyl fatty peroxyacid precursor compounds of the imide type include the N-,N,N^{1}N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Organic peroxyacids

The detergent compositions herein may contain as optional components of the bleaching system organic peroxyacids, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

Surfactant

The detergent compositions in accordance with the claimed invention preferably contain as an additional detergent component a surfactant selected from anionic, cationic, nonionic ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation of surfactant are from 1% to 35% by weight, most preferably from 1% to 20% by weight.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitteronic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

Essentially any anionic surfactants useful for detersive purposes can be included in the composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_6-C_{18} alkyl sulfates which have been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_6-C_{18} alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Anionic carboxylate surfactants suitable for use herein include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Preferred alkyl ethoxy carboxylates for use herein include those with the formula $RO(CH_2CH_2O)_x CH_2COO^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C_{13} or less, and the average x is from about 3 to 10 when the average R is greater than C_{13}, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C_{12} to C_{18} alkyl group.

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula
$RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R_1 or R_2 is a succinic acid radical or hydroxysuccinic acid radical, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Anionic secondary soap surfactant

An other type of soap surfactants are secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in

alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should preferably contain no ether linkages, no ester linkages and no hydroxyl groups. There should preferably be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 11-15 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the preferred secondary soap surfactants:

A. A highly preferred class of secondary soaps comprises the secondary carboxyl materials of the formula R^3 $CH(R^4)COOM$, wherein R^3 is $CH_3(CH_2)x$ and R^4 is $CH_3(CH_2)y$, wherein y can be O or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of (x + y) is 6-10, preferably 7-9, most preferably 8.

B. Another preferred class of secondary soaps comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R^5-R^6-COOM, wherein R^5 is C^7-C^{10}, preferably C^8-C^9, alkyl or alkenyl and R^6 is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note: R^5 can be in the ortho, meta or para position relative to the carboxyl on the ring.)

C. Still another preferred class of secondary soaps comprises secondary carboxyl compounds of the formula $CH_3(CHR)_k$-$(CH_2)_m$-$(CHR)_n$-$CH(COOM)(CHR)_o$-$(CH2)_p$-$(CHR)_q$-CH_3, wherein each R is C_1-C_4 alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion.

Especially preferred secondary soap surfactants for use herein are water-

soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactant

Essentially any nonionic surfactants useful for detersive purposes can be included in the compositions. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C_6-C_{18} fatty alcohols and C_6-C_{18} mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C_{10}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are

suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3; t is from 0 to 10, preferably 0, and X is from 1.3 to 8, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and -$(C_2H_4O)_XH$, where x is in the range of from 1 to 3.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

A suitable example of an alkyl aphodicarboxylic acid for use herein is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful herein include those compounds having the formula $R^3(OR^4)_XN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 18 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydyroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide

group containing from 1 to 3, preferable 1, ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{18} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions in accordance with the claimed invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Betaine surfactant

The betaines useful herein are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group or C_{10-16} acylamido alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl,m and R^2 is a C_1-C_5 hydrocarbyl group, preferably a C_1-C_3 alkylene group, more preferably a C_1-C_2 alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C_{12-14} acylamidopropylbetaine; C_{8-14} acylamidohexyldiethyl betaine; 4[C_{14-16}

acylmethylamidodiethylammonio]-1-carboxybutane; C_{16-18} acylamidodimethylbetaine; C_{12-16} acylamidopentanediethyl-betaine; [C_{12-16} acylmethylamidodimethylbetaine. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Sultaine surfactant

The sultaines useful herein are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group, more preferably a C_{12}-C_{13} alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl, and R^2 is a C_1-C_6 hydrocarbyl group, preferably a C_1-C_3 alkylene or, preferably, hydroxyalkylene group.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions herein. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched.

Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Water-soluble builder compound

The detergent compositions in accordance with the present invention preferably contain a water-soluble builder compound, typically present at a

level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, carbonates, bicarbonates, borates, phosphates, silicates and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less that about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Suitable silicates include the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate.

Silicates are preferably present in the detergent compositions in accord with the invention at a level of from 5% to 50% by weight of the composition, more preferably from 10% to 40% by weight.

Partially soluble or insoluble builder compound

The detergent compositions in accordance with the present invention may contain additionally a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. XH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeoilte MAP, Zeolite HS and mixtures thereof. Zeolite A has the formula

$Na_{12}[AlO_2)_{12}(SiO_2)_{12}]. xH_2O$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]. 276 H_2O$.

Heavy metal ion sequestrant

The detergent compositions herein preferably contains as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_3EDDS. Examples of such preferred magnesium complexes of EDDS include MgEDDS and Mg_2EDDS.

Enzyme

Another preferred ingredient useful in the detergent compositions in accord with the invention is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein.

A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention. By organic polymeric compound it is meant herein essentially any polymeric organic compound

commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent composition.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

Other suitable organic polymeric compounds include the copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 2,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions herein, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John.

Polymeric dye transfer inhibiting agents

The detergent compositions herein may also additionally comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

Optical brightener

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the composition herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

Clay mineral compound

The detergent compositions in accordance with the invention may contain as a fabric softening component a clay mineral compound, preferably present at a level of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition. For clarity, it is noted that the term clay mineral, as used herein, excludes sodium aluminosilicate builder compounds.

The weight ratio of clay mineral compound to any peroxyacid bleach precursor compound is preferably from 10:1 to 1:5, more preferably from 5:1 to 1:2, most preferably from 3:1 to 1:1.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $Al_2(Si_2O_5)_2(OH)_2.nH_2O$ and the compounds having the general formula $Mg_3(Si_2O_5)_2(OH)_2.nH_2O$. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites and sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure. Sodium or calcium montmorillonite are particularly preferred.

Suitable smectite clays, particularly montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minerals.

Clays for use herein preferably have a largest particle dimension of from 0.01μm to 800μm, more preferably from 1mm to 400 mm, more preferably from 5mm to 200 mm.

Particles of the clay mineral compound may be included as components of agglomerate particles containing other detergent compounds. Where present as such components, the term "largest particle dimension" of the clay mineral compound refers to the largest dimension of the clay mineral compound refers to the largest dimension of the clay mineral component as such and not to the agglomerated particle as a whole.

Substitution of small cations, such as protons, sodium ions, potassium ions, magensium ions and calcium ions, and of certain organic molecules inlcuding those having positively charged functional groups can typically take place within the crystal lattice structure of the smectite clays. A clay may be chosen for its ability to preferentially absorb one cation type, such ability being assessed by measurements of relative ion exchange capacity. The smectite clays suitable herein typically have a cation exchange capacity of at least 50 meq/100g. U.S. Patent No. 3,954,632 describes a method for measurement of cation exchange capacity.

The crystal lattice structure of the clay mineral compounds may have, in a preferred execution, a cationic fabric softening agent substituted therein. Such substituted clays have been termed 'hydrophobically activated' clays. The cationic fabric softening agents are typically present at a weight ratio, cationic fabric softening agent to clay, of from 1:200 to 1:10, preferably from 1:100 to 1:20. Preferred cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These may be present as distinct components or as components of the, hereinbefore

described, hydrophobically activated clay materials. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the detergent compositions in accord with the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Form of the compositions

The detergent compositions herein can be formulated in any desirable form such as powders, granulates, pastes, and tablets.

Solid compositions

The detergent compositions herein is preferably in the form of solids, such as powders and granules.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1200 g/litre.

Making processes - granular compositions

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

Laundry washing methods

The detergent compositions herein may be used in essentially any washing or cleaning method, including machine laundry washing methods.

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. The detergent can be added to the wash solution either via the dispenser drawer of the washing machine or by a dispensing device. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred washing method herein a dispensing device containing an effective amount of detergent product is introduced into the drum of a front-loading washing machine before the commencement of the wash cycle.

The dispensing device is a container for the detergent product which is used to deliver the product directly into the drum of the washing machine. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry

detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its immersion in the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use in accord with the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly know as the "granulette".

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangemnt to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Packaging for the compositions

Commercially marketed executions of the detergent compositions herein can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in copending European Application No. 93970141.4.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C_{12} alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C_{14}-C_{15} linear alkyl sulfate
CxyEzS	:	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7	:	A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25E3	:	A C_{12-15} branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5	:	A C_{12-15} branched primary alcohol condensed with an average of 5 moles of ethylene oxide
QAS	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$ - C_{14}
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA	:	C12-C14 topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate

Zeolite A : Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12} \cdot 27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers

NaSKS-6 : Crystalline layered silicate of formula δ-$Na_2Si_2O_5$

SKS-6/ Mn : Compound comprising NaSKS-6 doped with Mn^{++} ions at a doping level of 100 ppm prepared in accord with the preferred synthetic method as provided in the description

Citric acid : Anhydrous citric acid

Carbonate : Anhydrous sodium carbonate with a particle size between 200µm and 900µm

Bicarbonate : Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm

Silicate : Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)

Silicate/Mn : Compound comprising Silicate doped with Mn^{++} at a doping level of 100 ppm

Sodium sulfate : Anhydrous sodium sulfate

Citrate : Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850 µm

MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000

CMC : Sodium carboxymethyl cellulose

Protease : Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase

Alcalase : Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S

Cellulase : Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme

Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt.
TAED	:	Tetraacetylethylenediamine
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated bleach	:	Sulfonated Zinc Phthlocyanine encapsulated in dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
Brightener 47	:	Disodium 4-4'[(4-anilo-6-morpholino-s-triazin-2yl) -amino]-2'-stilbenedisulfinate
HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer

Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

Example 1

To test the performance of the detergent component of the present invention comparable split bundle performance laundry wash tests were done with different detergent compositions.

Test I was done with a detergent composition with formula A, as shown below. The reference used was a detergent composition with formula B, as shown below.

Test II was done with a detergent composition with the formula A, as shown below. The reference used was a detergent composition with formula C, as shown below.

	A	B	C
C45AS	6.84	6.84	6.48
C24E5	3.37	3.37	3.37
C25E3S	1.71	1.71	1.71
TFAA	1.45	1.45	1.45
Citric acid	2.45	2.45	2.45
Zeolite A	10.2	10.2	10.2
SKS-6/Mn	9.0	-	-

Carbonate	5.44	5.44	5.44
Silicate/Mn	-	-	9.0
NaSKS-6	-	9.0	-
Magnesium sulfate	0.6	0.6	0.6
Percarbonate	16.9	16.9	16.9
TAED	3.75	3.75	3.75
DTPMP	0.6	0.6	0.6
Endolase	0.25	0.25	0.25
Protease	0.69	0.69	0.69
Lipase	0.24	0.24	0.24
Cellulase	0.26	0.26	0.26
Amylase	0.6	0.6	0.6
MA/AA	3.6	3.6	3.6
CMC	0.31	0.31	0.31
Photoactivated bleach	20 ppm	20 ppm	20 ppm
Brightener 47	0.19	0.19	0.19
SRP	2.2	2.2	2.2

Perfume	0.35	0.35	0.35
Silicone antifoam	2.75	2.75	2.75
Minors/misc to 100%			

Test I

This test compared a detergent composition with formulation A with a detergent composition with formula B. The following wash conditions were used:

Washing conditions:
level of manganese : 1 ppm
in washing liquor
water hardness : 25 dH
temperature : 40°C
machine : AEG (trade name)
Usage based on : 100g detergent in 10 litres water

The following results were found:

A verses B (reference)

STAIN	40°C
Boil-in Coffee	+0.9
Boil-in Tea	+0.5
Overall Bleachable	+0.7

(results expressed on psu scale compared to the reference)

Test II

This test compared a detergent composition with formulation A with a detergent composition with formula C. The following wash conditions were used:

Washing conditions:
level of manganese : 1 ppm
in washing liquor
water hardness : 25 dH
temperature : 40°C
machine : AEG (trade name)
Usage based on : 100g detergent in 10 litres water

The following results were found:

A verses C (reference)

STAIN	40°C
Boil-in Coffee	+1.2
Boil-in-Tea	+1.4
Overall Bleacable	+1.0

(results expressed on psu scale compared to the reference)

The results show the benefits achieved related to improved bleachable stain removal by NaSKS-6 and manganese containing detergent component.

Example 2

The following laundry detergent compositions D to I were prepared in accord with the invention:

	D	E	F	G	H	I
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
SKS6/Mn	10.0	10.9	10.1	10.1	10.9	10.1
Sodium sulfate	16.0	16.0	16.0	16.0	16.0	16.0
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5.	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3

CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 3

The following granular laundry detergent compositions J to L of bulk density 750 g/litre were prepared in accord with the invention:

	J	K	L
LAS	-	5.61	4.76
TAS	-	1.86	1.57
C45AS	6.84	3.00	5.07
C24E5	3.37	-	5.0
C25E35	1.71	5.5	-
TFAA	1.45	2.0	2.0
Citric acid	2.45	-	-
Zeolite A	10.2	19.5	19.5
SKS-6/Mn	9.0	10.6	10.6
Carbonate	5.44	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	-	-	12.3
Magnesium sulfate	0.6	-	2.0
Percarbonate	16.9	12.7	-

TAED	3.75	3.1	-
DTPMP	0.6	0.2	0.2
Endolase	0.25	0.3	0.3
Protease	0.69	0.85	0.85
Lipase	0.24	0.15	0.15
Cellulase	0.26	0.28	0.28
Amylase	0.6	0.1	0.1
MA/AA	3.6	1.6	1.6
CMC	0.31	0.4	0.4
Photoactivated bleach	20 ppm	27 ppm	27 ppm
Brightener 47	0.19	0.19	0.19
SRP	2.2	0.04	0.04
Perfume	0.35	0.3	0.3
Silicone antifoam	2.75	2.4	2.4
Minors/misc to 100%			

Example 4

The following detergent formulations, according to the present invention were prepared, where M is a phosphorus-containing detergent composition, N is a zeolite-containing detergent composition and O is a compact detergent composition:

	M	N	O
Blown Powder			
STPP	12.0	-	12.0
Zeolite A	-	12.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
SKS-6/Mn	12.0	12.0	12.0
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.25	0.30	0.15

Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 5

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

	P	Q	R
Blown Powder			
Zeolite A	15.0	15.0	-
Sodium sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	-	3.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
SKS-6/Mn	12.0	12.0	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4

Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 6

The following detergent formulations, according to the present invention were prepared:

	S	T	U	V
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
SKS-6/Mn	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 7

The following detergent formulations, according to the present invention were prepared:

	W	X	Y
Blown Powder			
SKS-6/Mn	10.0	10.0	10.0
Zeolite A	20.0	12.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	14.0	12.0	12.0
C45AS	8.0	7.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
DTPMP	-	0.4	0.4
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	4.5
PB1	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

WHAT IS CLAIMED IS:

1. A detergent component comprising in combination

(a) a crystalline layered silicate; and

(b) a metal ion,

wherein said metal ion is present in the crystalline structure of said crystalline layered silicate.

2. A detergent component according to Claim 1 wherein the crystalline layered silicate is a crystalline δ-layered silicate.

3. A detergent component according to Claim 1 and 2 wherein the crystalline δ-layered silicate is a sodium silicate with the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20.

4. A detergent component according to Claim 3 wherein the crystalline δ-layered sodium silicate has the formula $Na_2Si_2O_5$.

5. A detergent component according to any of the preceding Claims wherein the crystalline layered silicate is present at a level from 5% to 30% by weight of the composition.

6. A detergent component according to any of the preceding Claims wherein said metal ion is selected from the group of transition metal ions consisting of manganese II, titanium IV, and mixtures thereof.

7. A detergent component according to any of the preceding Claims wherein the metal ion is present at a level from 10 ppm to 1000ppm by weight of the crystalline layered silicate.

8. A detergent component according to any of the preceding Claims wherein the detergent component contains the metal ion doped within the crystalline layered silicate structure.

9. A process for the preparation of a detergent component according to Claim 8 comprising the following steps

(1) forming a mixture containing the crystalline layered silicate, a metal salt and a solvent;

(2) refluxing said mixture;

(3) purifying the resultant product.

10. A detergent composition comprising

(a) an oxygen releasing bleach system;

(b) a detergent component according to any of Claims 1 to 8.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/03239

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C11D 3/02, 3/12, 7/02, 9/06, 9/18, 17/00
US CL :510/311, 376, 438, 508, 511
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/311, 376, 438, 508, 511.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	US 4,536,183 A (NAMNATH) 20 August 1985, abstract, col. 3, ll. 1-8, claims 1, 3, 7, 9, 14 & 16.	1 & 2
Y	US 4,820,439 A (RIECK) 11 April 1989, entire document in general, especially col. 2, ll. 44-52.	1 & 2
A	US 5,078,895 A (DANY et al.) 07 January 1992, entire document in general.	1 & 2

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 14 APRIL 1997	Date of mailing of the international search report 24 JUN 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer for ARDITH HERTZOG Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/03239

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS, CAS ONLINE
search terms: manganese?, titanium?, sks?, sks-6, deterg?, ?layersilicate?, ?layeredsilicate?, layer, layered, silicate#, 4664839, 4820439

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/03239

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1 ☐ Claims Nos..
because they relate to subject matter not required to be searched by this Authority, namely:

2 ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3 ☒ Claims Nos.. 3-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows.

1 ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos

4 ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.